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EFFECTS ON LDEF EXPOSED COPPER FILM AND BULK

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SUMMARY

Two forms of copper were exposed to the LDEF Mission 1 environment: a copper film initially 74.2 ± 1.1 nm thick sputter coated on a fused silica flat and a bulk piece of OFHC copper. The optical density of the copper film changed from 1.33 to 0.70 where exposed and the film thickness increased to 106.7 ± 0.5 nm where exposed. The exposed area appears purple by reflection and green by transmission for the thin film and maroon color for the bulk copper piece. The exposed areas increased in thickness, but only increase in the thickness of thin film sample could be readily measured. The increase in film thickness is consistent with the density changes occurring during conversion of copper to an oxide, however, we have not been able to confirm appreciable conversion to an oxide by x-ray diffraction studies. We have not yet subjected the sample to e-beams, or more abusive, investigations out of concern that the film might be modified.

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INTRODUCTION

The copper samples represent 2 of 64 cylindrical samples of 2.54 cm (1 inch) diameter that were flown on the leading, C9, tray of LDEF Mission 1 for 5 3/4 years of exposure in low Earth orbits. Matching trailing samples, which showed little effect, were located in the C3 tray. Appreciable effects on the copper were not anticipated, since active oxygen discharges on the ground for short periods had not shown the same gross degradation effects that silver had. The samples were mounted on ambient temperature surfaces believed to have had approximately room temperature values.

Copper oxide has a number of forms [1] ; two common forms of oxide are cuprite, Cu_2O , and tenorite, CuO . Cuprite has the properties: Molecular weight of 143.08, color is red, octahedral cubic structure, index of refraction of 2.705, and specific gravity of 6.0. The tenorite is black monoclinic, has a molecular weight of 79.54, index of refraction of 2.63, and specific gravity of 6.3 to 6.49. Copper has a molecular weight of 63.546, a cubic structure and a specific gravity of 8.92.

MEASUREMENTS

The copper samples were investigated by a number of techniques; these included: visual inspection by eye and optical microscope, photography, optical density measurements with visible white light using a scanning microdensitometer, thickness measurements by stylus profilometry, x-ray diffraction (XRD) electrical resistance measurements, ellipsometry, x-ray photoelectron spectroscopy (XPS), and profiling by optical interference techniques. We have not yet utilized scanning electron microscopy (SEM), Auger Electron Spectroscopy (AES), scanning Auger Microscopy (SAM), energy dispersive spectroscopy (EDS), or surface cleaning methods out of concern that we might modify the samples.

DISCUSSION

Visual inspection showed obvious changes to the exposed areas of both copper samples, as shown in Fig. 1. The bulk sample showed a maroon

discoloration, which did not change color with viewing angle, indicating that an interference film was not responsible for the color. The discoloration on the bulk sample was very-uniform in color. The thin film sample appeared basically purple when viewed off-normal and its reflectance and appearance were more poorly defined. By transmission the exposed area appeared green, and, while basically uniform, appeared to have small traces of inhomogenities.

Optical densitometry measurements showed considerable changes in the optical density in the visible; the unexposed copper film had an optical density of 1.33 and the exposed area had an optical density of 0.70. The changes in optical properties appear to be too great to be attributed to contamination, and the fact that contaminants on the trailing surface produced minor optical changes compared to the ram direction supports a model involving atomic oxygen interaction.

The stylus profilometry measurements were practical only on the thin film sample, because the discoloration changes were relatively thin. Changes on the order of 10's and 100's of nm are difficult to measure at steps on surfaces unless the steps are very sharp and the surface is very flat. Neither of these conditions could be satisfied for the bulk copper sample; attempting to remove fine scratches of discoloration would also scratch the underlying copper; also, steps at the knife edges of the masking cover were not distinct enough to separate them from the uneven surface of the polished, but not flat copper disk. The thin copper film of 74.2 ± 1.1 nm initial thickness, however, was deposited on a fused silica flat and both the unexposed and exposed areas were easily scratched with fine lines near the mask boundary, exposing bare silica. The square negative pulse-like traces gave good indications of the thicknesses of exposed and unexposed regions at several locations around the mask perimeter. The average thickness in the exposed area was 106.7 ± 0.5 nm. Measurements at the mask edges gave a height of the step equal to an average of 34.3 nm, in agreement with the difference in total film thicknesses.

Using literature values [1] for the copper and its oxide and assuming that film expansion occurs normal and not lateral to the surface, we can estimate what should happen to film thickness if copper is converted to an oxide. Taking the reciprocal of the copper density and multiplying this by the molecular weight and dividing by Avogadro's number gives 1.183×10^{-23} cm³/atom as an estimate for each atom. Since film densities are usually not exactly the same as bulk densities, this is only an

approximation, but taking the cube root of this value gives 2.28×10^{-8} cm, with which we can estimate the number of copper atoms in our 74.2 nm thick film, i.e. over a 1 cm² area we should have about 325 atomic layers and about 6.25×10^{17} copper atoms. One-half as many Cu₂O molecules can be formed from these copper atoms; thus, finding the cm³/molecule for Cu₂O, as before, and multiplying by 3.13×10^{17} molecules gives 1.24×10^{-5} cm³, or 124 nm thickness over the 1 cm² area. Similar calculation for CuO gives 129 nm over a 1 cm² area. Comparing these values to the measured value of 106.7 nm, indicates that partial conversion to either oxide would expand the copper sufficiently to give the measured value for the exposed material. X-ray diffraction results so far suggest free copper predominates both exposed and unexposed areas and only hints at the presence of Cu₂O, as shown in Fig. 2; however, these studies are very difficult because of the thinness of the film and further studies designed for thin films may improve the results.

Electrical resistance measurements were performed with two probe contacts at only a couple of locations, since soldering or outer bonding techniques were not allowed, and minimal contact with the surface was desired. Values of less than 100 ohms per square were obtained in the exposed area, which was orders of magnitude higher than in the unexposed area. No temperature dependent measurements to confirm metallic or semiconducting properties have been performed yet. Resistance calculation for a copper film 74.2 nm thick gives 0.23 ohms/square, which is also the order of accuracy of the two contact measurements used.

Ellipsometry measurements were attempted on the exposed surfaces with disappointing results; as with previous attempts to measure the optical properties of silver oxide, no definitive results were obtained. We have not determined the cause of the difficulty, but suspect overlying contamination and perhaps inhomogeneity in the film itself as possible reasons for failing to get good results.

XPS measurements were carried out using Mg K α X-rays (1253.6 eV) as the excitation source. Three specimens (two thin films, C3-16 and C9-16, and one bulk, C9-30) were analyzed which showed varying degrees of surface contamination and the atomic concentrations of all the species on these surfaces are shown in Table 1. Cu 2p core level was used to characterize the presence of Cu₂O and CuO in addition to X-ray excited Cu L_{2,3}M_{4,5}M_{4,5} Auger lines. It has been shown previously [2 and references therein] that Cu 2p_{3/2} from CuO is relatively broad and is

accompanied by a satellite on the high binding-energy side at about 9 eV and is due to the multiplet splitting in the $2p^53d^9$ final state. The Cu $2p_{3/2}$ peak from Cu_2O has a single peak which is considerably narrower and closely resembles the peak from metallic Cu. On the bulk Cu sample we obtained Cu 2p peak resembling CuO in the exposed and metallic Cu in unexposed regions, respectively. However, on the thin film specimens, only single Cu $2p_{3/2}$ peak was obtained in both exposed and unexposed regions which may be construed as indicating the presence of pure copper or Cu_2O species on the surface. This is supported by x-diffraction results discussed above. The Cu $L_{2,3}M_{4,5}M_{4,5}$ Auger spectra of CuO and Cu_2O show distinct differences and their spectral shapes are considerably different. This will be discussed in detail elsewhere [3].

Eventually partial cleaning of small areas of the surfaces may be attempted by low flux argon ion bombardment through apertures, enabling profiling the film thickness, but this partially destructive technique will be delayed until other approaches have been exhausted.

Profiling the surface by optical interference techniques works best when the whole surface has similar optical properties, with preferably high reflectance. The results on the two halves with greatly different optical properties were poor, compared to the mechanical stylus profiles.

Scanning electron microscopy and energy dispersive spectroscopy will eventually be tried on a turbo pumped SEM system and perhaps with limiting apertures again. While these techniques should provide very useful results, especially on an EDS system with thin window capable of analyzing oxygen x-rays, it is important to be cautious, since electron beams can polymerize some materials like pump oil and break some bonds in other materials. We wish to investigate the surfaces further before taking these steps.

While selective modification occurred only in the ram direction, expansion of the exposed film was consistent with partial conversion to an oxide, and other supportive evidence suggests that the copper was modified by heavy oxidation in the areas exposed to the orbital ram. We lack full confirmation that this is the cause at this time.

REFERENCES

- 1 : "Physical Constants of Inorganic Compounds", Handbook of Chemistry and physics, P. B87-89, 52 Edition (1971), Ed. Robert C. Weast, The Chemical Rubber Co, Cleaveland, Ohio
- 2 : J. Ghijsen, L.H.Tseng, J. van Elp, H. Eskes, J. Westerink, G.A.Sawatzky, and M. T.Czyzk, Phys. Rev. B38 (1988) 11322
- 3 : G.N. Raikar, J.C.Gregory and P.Peters (in preparation)

FIGURE CAPTION

Figure 1: Photograph of the bulk and thin film copper samples from C9 tray

Table 1

| Atomic Concentration | | | | | | |
|----------------------|-----|------|------|----|-----|-----|
| Unexposed Region | | | | | | |
| Element | Cu | O | C | Si | Na | Cl |
| C3-16 | 6 | 21 | 67 | 5 | 0 | 1 |
| C9-16 | 3 | 21.5 | 66 | 9 | 0 | 0.5 |
| C9-30 | 5.5 | 25 | 63 | 5 | 0.5 | 1 |
| Exposed Region | | | | | | |
| Element | Cu | O | C | Si | Na | Cl |
| C3-16 | 9 | 23 | 62.5 | 4 | 0.5 | 1 |
| C9-16 | 4 | 37.5 | 44.5 | 14 | 0 | 0 |
| C9-30 | 9 | 55 | 18.5 | 17 | 0 | 0.5 |



Fig. 1.